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(continued on next page)

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US 4454207 A
US 4374184 A
US 20010010873 A1

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(54) Abstract Title: **Method and device for operating an immediate temperature solid oxide fuel cell**

(57) A method and apparatus for operating an intermediate temperature solid oxide fuel cell using methanol as a fuel. Methanol is reformed to produce hydrogen which is supplied to an anode of the fuel cell. The temperature at which methanol is reformed (about 300°C) is very well suited to use with an intermediate - temperature solid oxide fuel cell which generally operates within the temperature range 450-650°C as the evaporation of the fuel and water mix, as well as the reforming reaction can be used to cool the fuel cell. Cooling using a larger temperature difference would impose an excessive thermal shock on a fuel cell apparatus or stack.

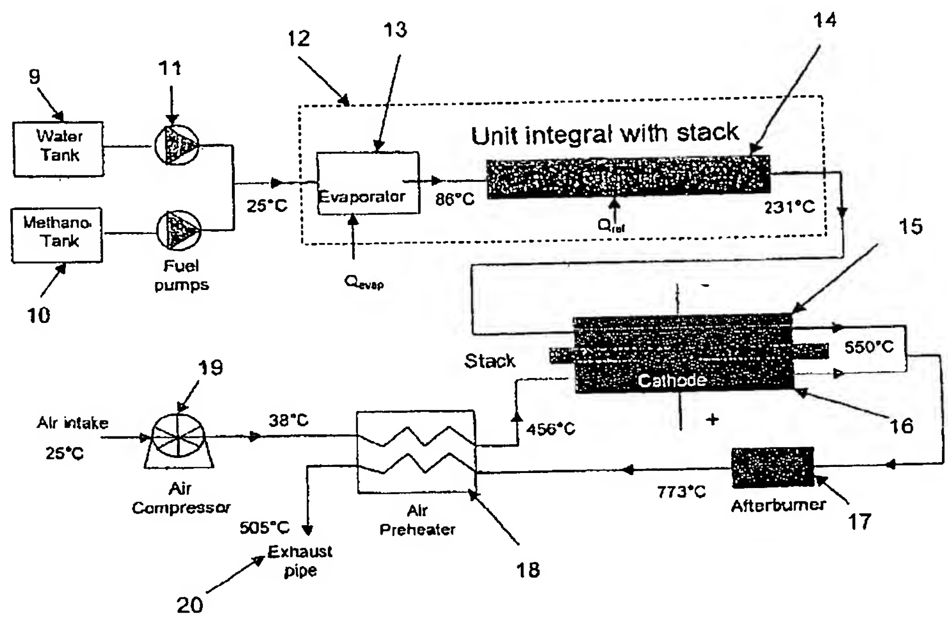

Figure 3

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GB 2405028 A continuation

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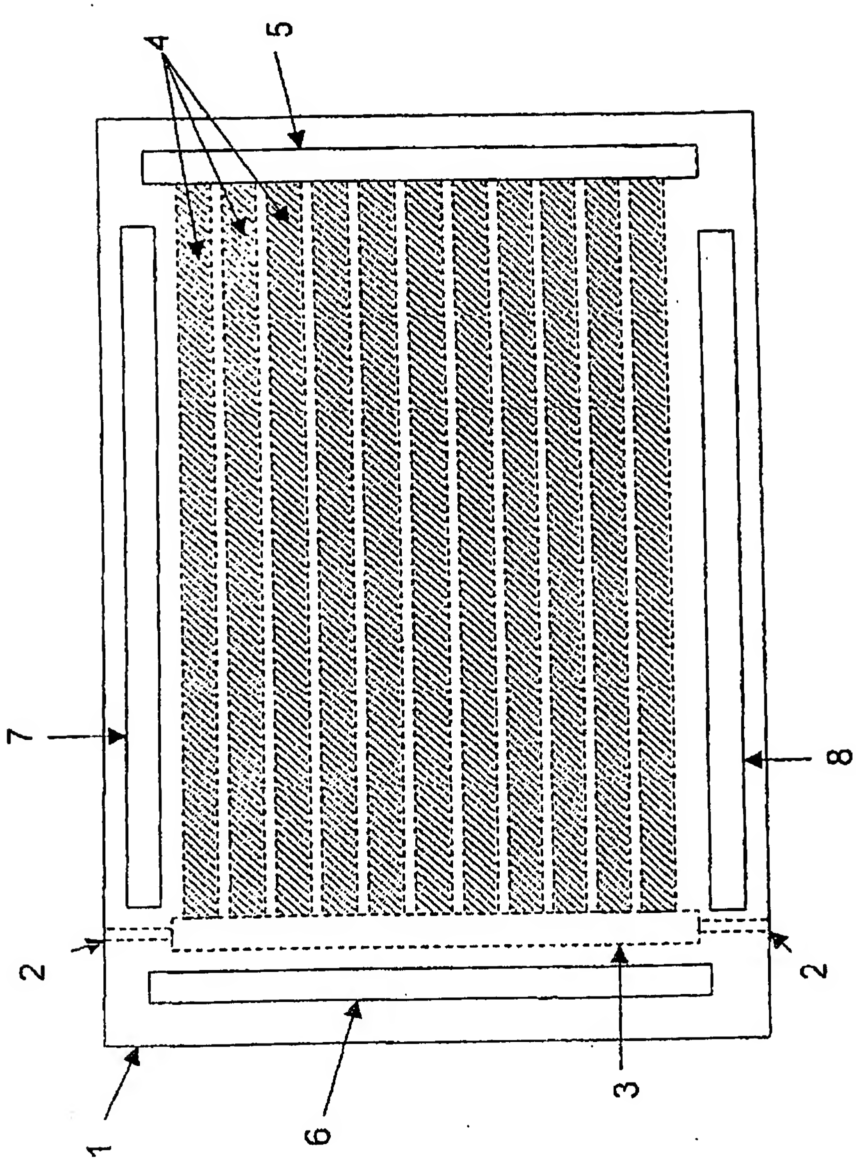


Figure 1

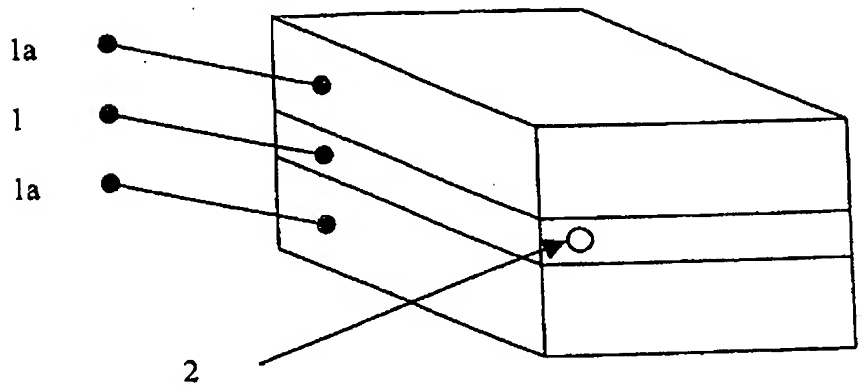
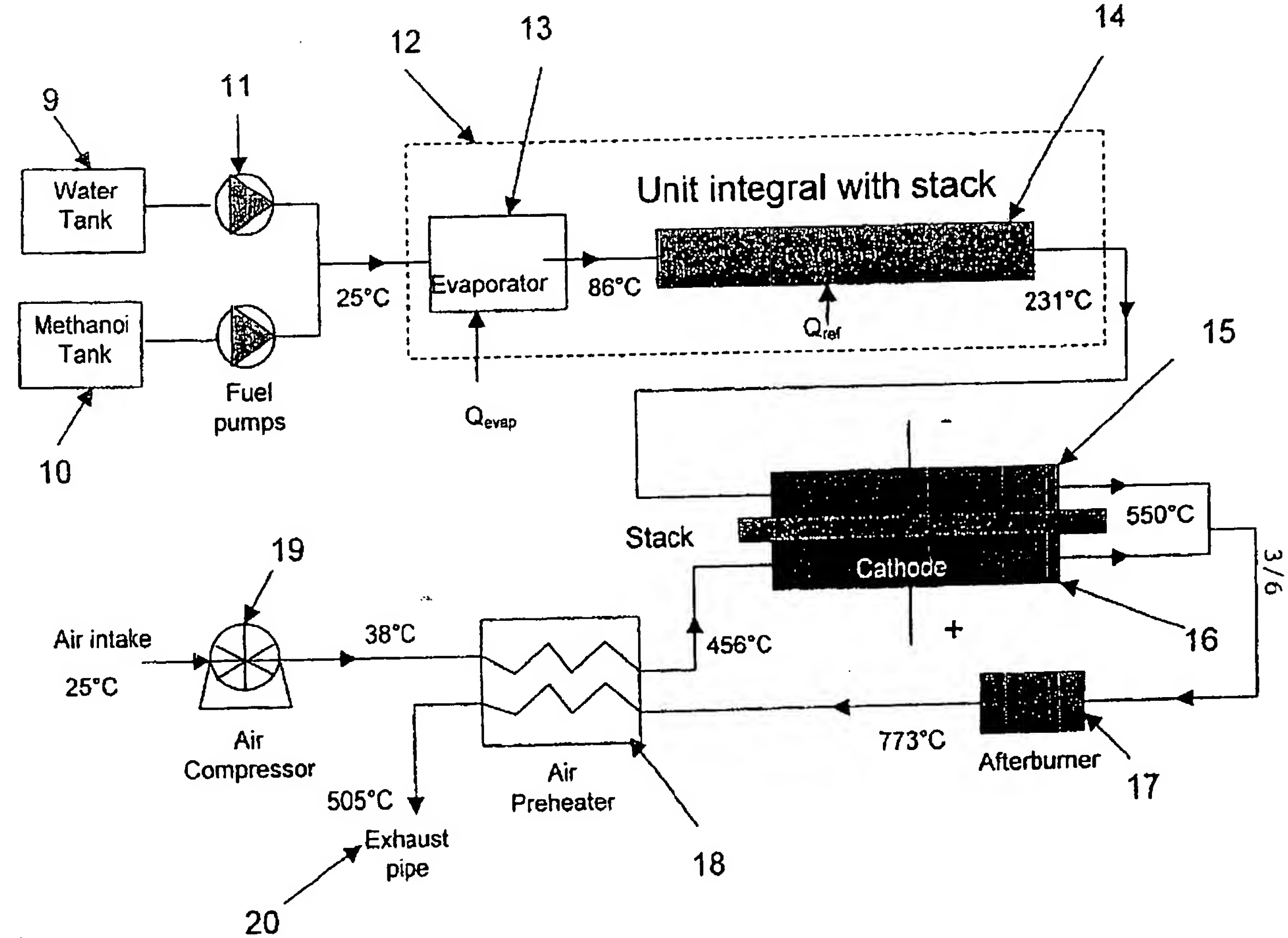


Figure 2



9
10
11
12
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15
16
17
18
19
20
Water Tank
Methanol Tank
Fuel pumps
25°C
Evaporator
Q_evap
86°C
Unit integral with stack
Q_ref
231°C
Stack
Cathode
-
+
550°C
3/6
Afterburner
773°C
Air intake
25°C
Air Compressor
38°C
Air Preheater
456°C
505°C
Exhaust pipe

Figure 3

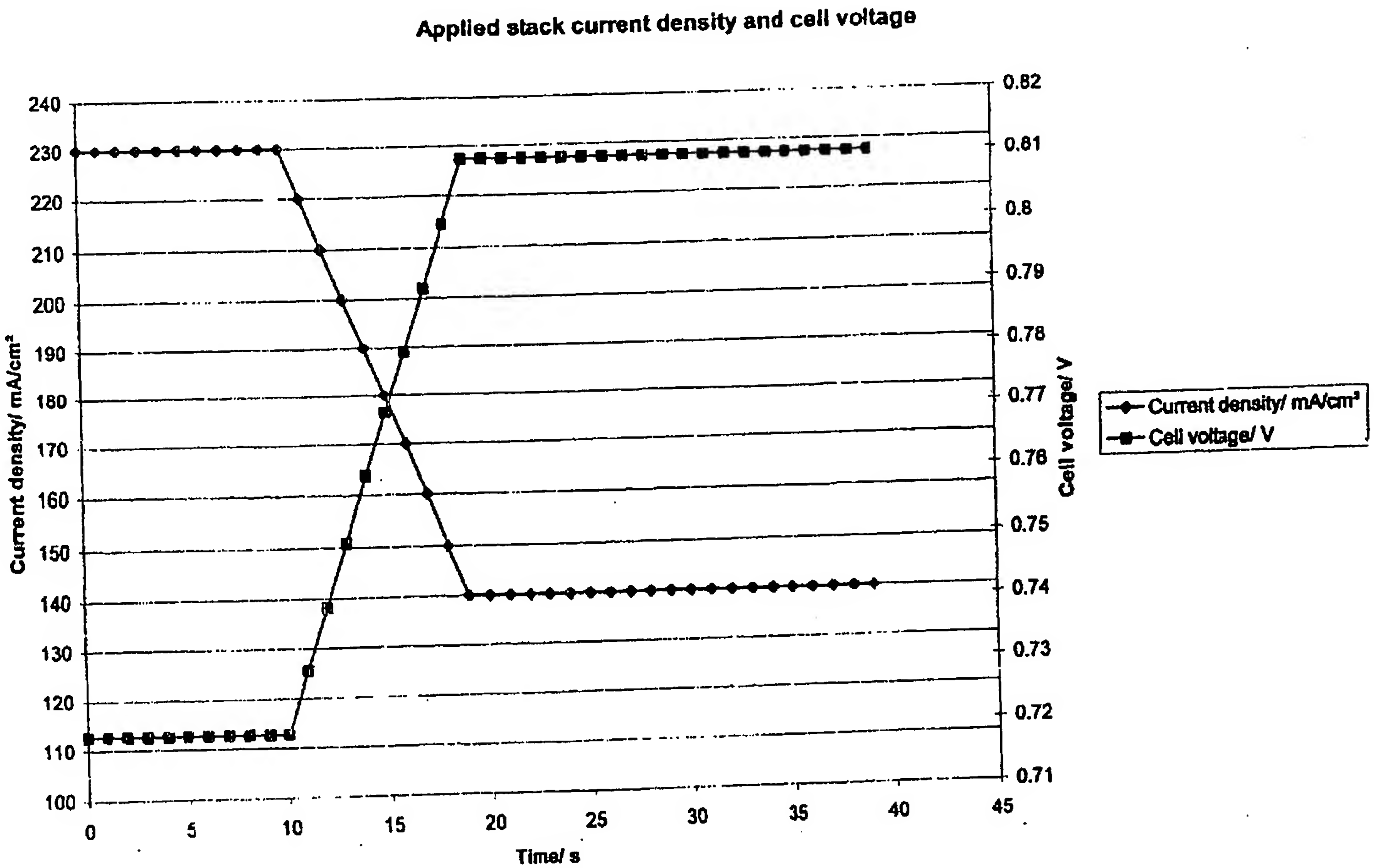
Applied stack current density and cell voltage
Current density/ mA/cm²
Cell voltage/ V
Time/ s
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
0.82
0.81
0.8
0.79
0.78
0.77
0.76
0.75
0.74
0.73
0.72
0.71
0
5
10
15
20
25
30
35
40
45
Current density/ mA/cm²
Cell voltage/ V

Figure 4

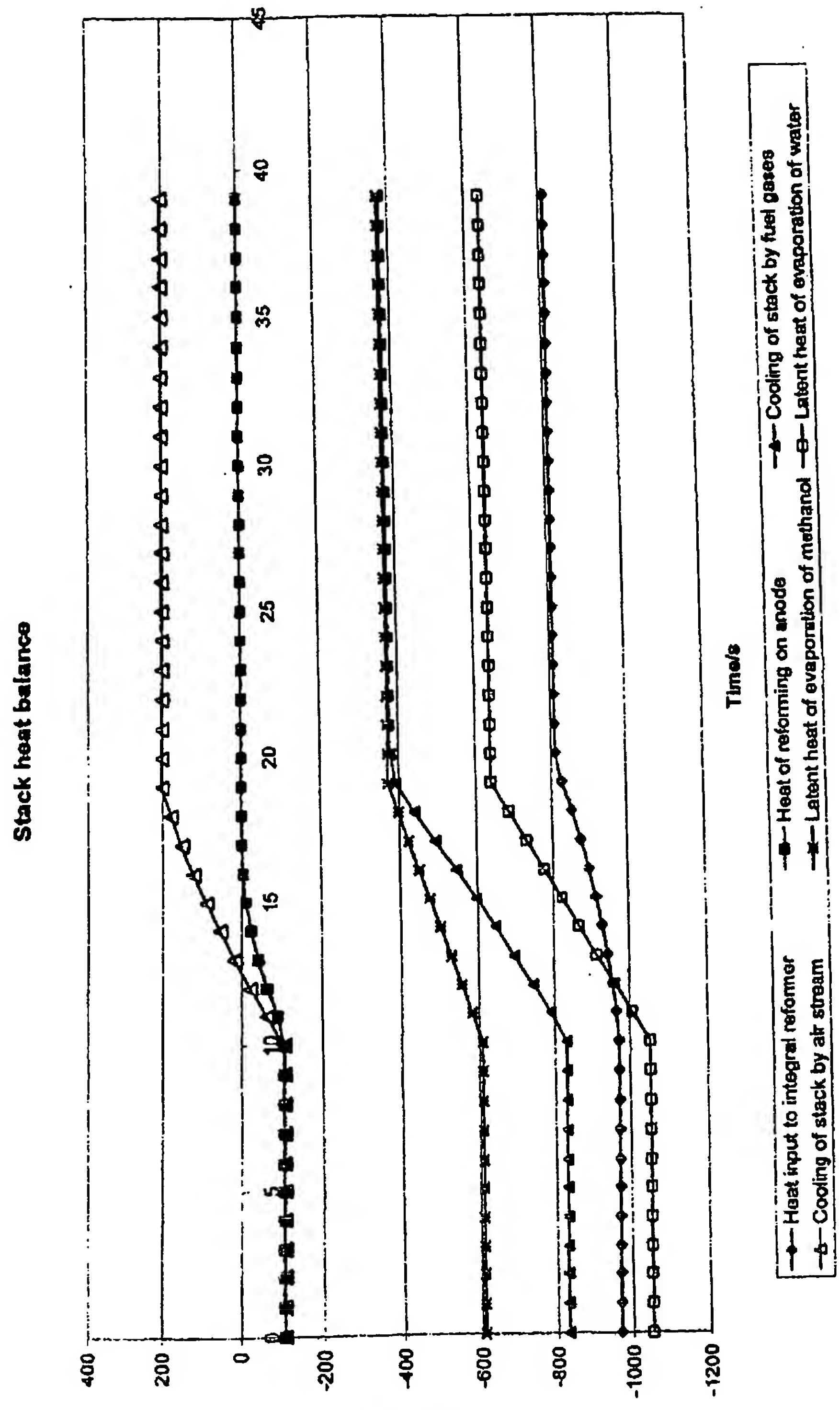
Stack heat balance
Power (heat) / W
400
200
0
-200
-400
-600
-800
-1000
-1200
0
5
10
15
20
25
30
35
40
45
Time/s
Heat input to integral reformer
Heat of reforming on anode
Cooling of stack by fuel gases
Cooling of stack by air stream
Latent heat of evaporation of methanol
Latent heat of evaporation of water

Figure 5

Predicted system performance	Value
DC electrical efficiency (LHV basis) / %	52
Net AC electrical efficiency (including parasitic losses)/ %	44
DC electrical power/ kW	5.0
AC electrical power/ kW	4.25
Stack voltage/ V	151.2
Applied current/ A	33.1
Fuel utilisation/ %	85
Stoichiometric air ratio	2.5
Specific CO_2 emissions/ $gkWh_e^{-1}$	520

Figure 6

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Method and device for operating an intermediate temperature solid oxide fuel cell

FIELD OF THE INVENTION

This invention relates to a method and an apparatus for the operation of an intermediate temperature solid oxide fuel cell (IT-SOFC).

BACKGROUND OF THE INVENTION

A fuel cell is an electrochemical device for the conversion of the chemical energy in a fuel (often but by no means exclusively hydrogen gas) into direct-current electrical energy. By comparison with more conventional means of achieving this energy conversion, fuel cells offer the potential of high conversion efficiency and low environmental pollution.

There are many different types of fuel cell. This invention refers specifically to intermediate temperature solid oxide fuel cells, an example of which is described in the publication WO 02/35628. This type of fuel cell comprises an anode, a cathode and an electrolyte sandwiched in between. A fuel gas (typically hydrogen and or carbon monoxide) is fed to the anode, and an oxidant (usually air) to the cathode. Oxygen is reduced at the cathode, and then conducted through the electrolyte to the anode side as oxide ions. These oxide ions then combine with the fuel gas on the anode side, producing steam or carbon dioxide as reaction products. The electrolyte material in this fuel cell is typically an oxide-ion conducting ceramic material such as cerium gadolinium oxide (CGO). In this particular type of fuel cell the ceramic layers are deposited as thick films over a porous metallic substrate, which provides mechanical support for the fragile ceramics. The use of a metal support and a highly oxide ion conducting electrolyte allows the fuel cell to operate at a comparatively low temperature of between 500°C and 600°C. Operating in this temperature range has several benefits when compared to more conventional SOFC technology which operates in the 700-1000°C range. These advantages include more rapid heating and cooling of the fuel cell stack, the ability to use lower-cost materials, and greatly reduced material degradation problems. The use of metal supports also enables the use of metal-to-metal seals to be used within the stack, greatly reducing the problems associated with the metal-to-ceramic seals found in more conventional SOFCs.

To produce useful amounts of power, a number of individual fuel cells are typically arranged together on a sheet or several sheets in a stack comprising a means of feeding gas to the cells, and withdrawing an electrical current from them. The cells referred to in the present invention are preferentially arranged in, but not limited to, a planar arrangement with metallic interconnect plates.

Fuel cells in general operate most effectively utilising low molecular weight gases such as hydrogen and carbon monoxide as fuels. However, these gases are rarely available as a convenient fuel source, since most presently readily available fuels are hydrocarbon based, and will remain so for the foreseeable future. One frequently adopted option to enable fuel cells to be operated efficiently on readily available hydrocarbon fuels is steam reforming. In this process, a hydrocarbon is reacted to form a hydrogen/carbon monoxide mixture through high temperature reaction with steam. This hydrogen/carbon monoxide mixture is then fed to the anode compartment of the fuel cell. Fuels suitable for steam reforming include but are by no means limited to natural gas, LPG, methanol, ethanol and gasoline. The steam reforming reaction of most of these fuels is highly endothermic, requiring a source of high-grade heat to drive the reaction. Solid oxide fuel cells, with their high operating temperature, produce high-grade waste heat as a by-product of normal operation. This means that, by comparison with lower temperature fuel cells, solid oxide fuel cells can be operated on commonly available hydrocarbon or alcohol fuels without an appreciable loss of overall efficiency by comparison with operation on pure hydrogen. By comparison, lower temperature fuel cells require the combustion of a fraction of the supplied fuel to generate enough heat to drive the reforming reaction. This invariably reduces the overall efficiency. Also, solid oxide fuel cells are tolerant of carbon monoxide in the fuel gas, whereas in low temperature fuel cells carbon monoxide poisons the anode, and thus has to be removed from the reformate.

Solid oxide fuel cell stacks typically achieve an internal energy conversion efficiency of 30-70%. This means that 70-30% of the available energy in the fuel gas is dissipated as heat within the stack. Stacks operating at a power level above that where this heat is lost naturally to the environment require cooling to maintain a constant operating temperature. This is typically achieved by means of feeding substantially more air to the stack than is actually required by the chemical reaction. However, this means of cooling alone is inefficient, since much electrical energy is required to drive a compressor to force the air through the stack and surrounding

components. This represents a significant parasitic loss which affects the overall efficiency of the system. In addition, the air fed to the stack needs to be heated to within 200°C, or more preferably within 150°C of the stack temperature, since air fed at ambient temperature would impose too great a thermal shock on the stack. This air heating is typically performed by means of a heat exchanger recovering waste heat from the stack exhaust stream. If a large volume of air needs to be fed to the stack, this heat exchanger becomes a large and potentially very expensive component in any such system.

To reduce the amount of air required for cooling of the SOFC stack, it is common to at least partially perform the steam reforming of a hydrocarbon fuel within the stack, using the endothermic nature of the reforming reaction to directly consume waste heat within the stack. This is known as internal reforming, and can be either direct (fuel is reformed directly on the fuel cell anode) or indirect (fuel is reformed on a separate catalyst pack built into the stack assembly). Those skilled in the art will be aware that the high operation temperature of most conventional SOFCs precludes the internal reforming of hydrocarbon fuels other than methane, since most other, less stable hydrocarbon molecules tend to decompose and deposit carbon within the stack, thus degrading the anode. However, at the operation temperature of the IT-SOFC stack to which this invention refers, much greater flexibility in internal reforming is possible because the operating temperature is below that at which most commonly available fuels will decompose.

OBJECT OF THE INVENTION

It is the object of this invention to provide a method for the efficient operation of an IT-SOFC.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention there is provided a method of operating an intermediate-temperature solid oxide fuel cell (IT-SOFC) comprising an anode and a cathode separated by an electrolyte, the method comprising:

operating the fuel cell at between 450 and 650°C,

using the evaporation of the methanol and water fuel mixture within the stack, or evaporator, or reformer unit to cool the IT-SOFC,

reforming methanol to generate hydrogen for use by the anode and

using the reforming reaction to cool the IT-SOFC.

The internal reforming of methanol proceeds according to the following reaction.

$$CH_3OH_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + 3H_{2(g)} \quad (1)$$

This reaction is not particularly endothermic, with a reaction enthalpy of 49 $kJmol^{-1}$, proceeding readily to completion at around 300°C over a suitable catalyst such as CuZnO.

The temperature at which methanol is reformed (about 300°C) is very well suited to association with an IT-SOFC which generally operates within the range 450 to 650°C as the reforming reaction can be used to cool the fuel cell.

The method of operating an IT-SOFC system of the invention may involve methanol being reformed in a reformer in thermal contact with the fuel cell, such as by the reformer being provided within a fuel cell stack. Alternatively or additionally a methanol/water mixture may be reformed in an anode compartment of a fuel cell or fuel cell stack. A mixture of typically 1.0 to 2.0 moles of water for every 1 mole of methanol may be fed and injected, preferably as a fine mist, into one or more reformers built into the fuel cell stack and/or an anode compartment of the fuel cell. The injection of the fuel as a fine mist is preferable to ensure rapid and even evaporation, but other methods of fuel injection are possible within the scope of this invention.

An evaporator and reformer unit within a stack uses the heat generated within the stack to first evaporate and then reform the fuel mixture. In so doing, the evaporation and then reforming processes both provide a substantial degree of internal cooling to the fuel cell stack, thus reducing the requirement for air cooling of the stack, and improving the system efficiency.

A methanol-water mixture may be evaporated and then reformed to a hydrogen-rich gas, containing 40-80 mole% hydrogen, with the remainder made up of steam, carbon dioxide and small amounts of carbon monoxide. This gas may then be fed to the anodes of the fuel cell stack, where it is partially consumed in the cell reaction, with most of the hydrogen converted to steam.

Instead of a reformer being provided within the fuel cell stack, it could be provided separately but in thermal contact with the fuel cell or with suitable means provided to convey heat generated by the fuel cell to the reformer. Alternatively or additionally the reforming of the methanol could be performed within an anode compartment of the fuel cell or a fuel cell stack.

Those skilled in the art will appreciate that it is very difficult to consume all the fuel in an SOFC stack, so there will always be some residual hydrogen in the anode off-gas.

In a preferred embodiment, the anode off-gas containing residual hydrogen, and the cathode off gas of oxygen-depleted air are mixed together and fed to a catalytic afterburner. In this afterburner the residual fuel is burned, resulting in a high temperature exhaust gas stream. The hot exhaust from the catalytic afterburner is used to preheat the incoming air via a heat exchanger, heating the incoming air from near ambient to within 200°C, or more preferably within 150°C, of the stack temperature prior to it being fed to the cathode side of the stack. The exhaust stream leaving the air preheater still contains substantial heat, and could in one advantageous embodiment be fed to a second heat exchanger, where waste heat could be recovered as part of a combined heat and power system.

The air supply for the stack is preferentially provided by an electrically powered compressor, which advantageously has a variable-speed motor enabling the supply of air to be controlled. However, a supply of compressed air could also be used if this were conveniently available from some other source.

According to a second aspect of the present invention there is provided an intermediate-temperature solid oxide fuel cell system comprising:

an intermediate-temperature solid oxide fuel cell including an anode and a cathode separated by an electrolyte;

a reformer for reforming methanol to generate hydrogen to be supplied to the anode and

the fuel cell and reformer being arranged such that heat generated by the fuel cell when in use is conveyed to the reformer.

The reformer may be arranged within a stack of fuel cells such that heat from the fuel cells is conveyed to the reformer. Alternatively or additionally the reformer may be arranged in thermal contact with the fuel cell or means may be provided to convey heat generated by the fuel cell to the reformer, such as one or more conduits

arranged to convey fluid therebetween. The reformer may be provided in an anode compartment of the fuel cell or a fuel cell stack.

A specific example of the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 shows one possible embodiment of an internal evaporator and reformer, although this is in no way intended to limit the scope of the invention to this specific embodiment;

Figure 2 shows a reformer in a fuel cell stack;

Figure 3 is a flow diagram of an apparatus illustrating an example of the invention;

Figure 4 is a graph of the predicted current density and cell voltage for the embodiment illustrated in figure 3, based upon computer simulations;

Figure 5 is a graph of the heat balance within the stack for the embodiment illustrated in figure 3, from the same computer simulation as figure 4 and

Figure 6 is a table illustrating a typical predicted set of performance values for the embodiment illustrated in figure 3.

Referring to figure 1, the evaporator/reformer shown in this example is a metallic plate 1 with high thermal conductivity. This plate is internally hollow. The liquid water/methanol mixture is introduced through side passages 2 into an evaporation chamber 3. When provided within a fuel cell stack, the temperature within the evaporator/reformer is such that the liquid should boil virtually instantly, producing a vapour mixture at around 86°C. The vapour mixture then enters internal channels 4 containing a reforming catalyst. During the passage of the vapour through these channels, the mixture is heated rapidly to a temperature in the range 200-350°C, more preferentially in the range 230-260°C, after which the reforming reaction begins to occur rapidly, ensuring close to full conversion of the methanol to hydrogen and carbon dioxide by the ends of the channels 4. The resulting hydrogen-rich gas is discharged into a fuel gas manifold 5, from where it is distributed to fuel cell anodes in a fuel cell stack assembly.

In one embodiment, one or more of the evaporator/reformer plates 1 described and illustrated in figure 1 are built into a fuel cell stack as shown in figure 2, so as to maintain as homogeneous a vertical temperature profile in the stack as possible, with the evaporator/reformer plates 1 acting as an internal heat sink. In the example of the fuel cell stack shown in figure 2 the evaporator/reformer plate 1 is provided with a

fuel cell arrangement 1a above and below it. Further fuel cells and/or evaporator/reformers may be provided above and/or below those illustrated in Figure 2. Additional manifolds are built into the plate 1, for fuel exhaust 6 and air feed 7 and exhaust 8. It should be apparent to those skilled in the art that many other configurations of the same basic concept as that illustrated in figures 1 and 2 are possible depending upon the stack design. It should be understood that various changes and modifications may be made without departing from this novel concept.

Figure 3 is a flow diagram of an apparatus illustrating an example of the invention. The apparatus consists of a water tank 9 and a methanol tank 10. However, in another related embodiment the water and methanol could be premixed and stored in a single tank, or multiple tanks, and piped directly. Both water and methanol (or a mixture) are fed to the stack unit by means of a pump 11 and metering valve (not illustrated), or alternatively by means of a metering pump. This system enables the rate of fuel supply to the stack unit to be controlled, based upon the applied or desired fuel cell current. The methanol/water mixture is fed into an evaporator 13 inside the stack, such as that illustrated in figure 1. The resulting methanol vapour/steam mixture is then fed to a reformer catalyst bed 14, also integral with the stack, and converted to a hydrogen-rich reformate, containing 60-70 mol% hydrogen. The hydrogen rich gas is fed to an anode compartment 15 of the fuel cell stack, where much of the hydrogen is consumed in the cell reaction. Typically 20-85% of the hydrogen is consumed within the stack reaction. More preferentially 70-85% of the hydrogen is consumed within the stack reaction, but under start-up and low-power operation this may be lower.

The anode and cathode exhaust gases are mixed and fed to a catalytic afterburner 17 where the residual hydrogen in the exhaust gas is burned, producing a gas stream at up to 800°C. This gas stream is then fed to the air preheater 18 where it is used to preheat the incoming air. The exhaust gas can then either be vented to atmosphere 20 or alternatively the residual heat in the exhaust gas stream can be recovered as part of a combined heat and power (CHP) system (not shown).

Air for the fuel cell cathode reaction is fed by a rotary compressor 19, which in an advantageous embodiment has a variable speed motor and a downstream flow meter, so the supply of air can be controlled to achieve the desired stack operating parameters. Those skilled in the art will be aware that it is usual in SOFC systems to feed at least double the amount of air required for the electrochemical reaction, so as

to minimise the danger of voltage losses due to oxygen starvation. In this invention, at least double the stoichiometric air requirement (lambda) is fed to the stack, with any excess above a lambda of 2.0 used to provide additional cooling of the stack. However, upon simulation of the operation of the apparatus, lambda values of greater than 2.5 were not required to maintain the stack at a constant temperature. This may be contrasted with systems without the reforming system described in this invention, where lambda values of 6.0 or more are often required. Those skilled in the art will appreciate the significant reduction in parasitic power loss for compression this represents, and thus the improvement in overall system efficiency. The actual saving in compressor power depends upon the back pressure against which the flow of air has to be driven, which depends upon the design of various stack and system components. However, for any given system design increasing the air flow will increase the back pressure, thus requiring a larger flow to be compressed to a higher pressure. Thus the increase of parasitic power loss with lambda is non-linear.

The air leaving the compressor is then heated in the air preheater 18 to around 450°C prior to being fed to the stack.

Figures 4-6 illustrate results of a dynamic computer simulation of a 5 kW_e embodiment of the system, to illustrate the viability of the invention.

Figure 4 shows the current density and predicted cell voltage during a simulation where the current density was initially applied at 230 $mAcm^{-2}$, giving a total stack power output of 5 kW DC. The current density was then ramped down with time to 140 $mAcm^{-2}$, with the fuel and air supplies reduced proportional to the current.

Figure 4 illustrates the predicted cell voltage as the current on the modelled stack is reduced.

Figure 5 illustrates the sources of cooling within the modelled stack, generated during the same simulation as figure 4. It can be seen that the majority of the stack cooling load is provided by the evaporation and reforming of the fuel. At full power, 1051 W of heat is required to evaporate the water feed, and 609 W is required to evaporate the methanol. A heat input of 971 W is required for the reforming of the fuel gases and to heat the vapour mixture to 230°C. At full power the fuel mixture is not completely reformed to hydrogen within the indirect internal reformer, with some residual methanol converted within the stack on the anode surface. This requires a heat input of 103 W. Heating of the fuel gases from 230°C to the full stack operating

temperature of 550°C requires a further 830 W. This leaves just 100-200W of cooling to be provided by the air stream.

Figure 6 shows the predicted performance levels of this system, demonstrating excellent predicted overall efficiency in spite of the very simple balance of plant.

Many variations may be made to the example described above whilst still falling within the scope of the invention. For example instead of or in addition to the reformer 1 being provided in a fuel cell stack, the reformer could be provided in thermal contact with a fuel cell unit, for example by being provided adjacent to the fuel cell unit. Alternatively or additionally means may be provided to convey heat generated by a fuel cell unit to a reforming unit, for example via fluid in one or more conduits interconnecting a reforming unit and a fuel cell unit.

If desired the reforming reaction may take place in an anode compartment of the fuel cell in addition to or as an alternative to reforming in a reformer. Methanol would then be supplied to the anode compartment and a suitable reforming catalyst would preferably be provided in the anode compartment.

CLAIMS

1. A method of operating an intermediate-temperature solid oxide fuel cell (IT-SOFC) comprising an anode and a cathode separated by an electrolyte, the method comprising:

operating the fuel cell at between 450 and 650°C,

reforming methanol to generate hydrogen which is supplied to the anode of the fuel cell and

the reforming reaction being arranged to receive heat generated by the fuel cell and

the use of both evaporation of the methanol fuel and water, and the fuel reforming process to cool the IT-SOFC.

2. A method according to claim 1, wherein the reforming reaction is performed in a reformer unit which is arranged in contact with the fuel cell such that in use heat generated by the fuel cell is conveyed to the reforming reaction.

3. A method according to claim 2, wherein the reformer is provided within a fuel cell stack.

4. A method according to claim 3, wherein a plurality of reformers are provided in a fuel cell stack.

5. A method according to claim 1, wherein the reforming reaction is performed in a reformer and means are provided to convey heat generated by the fuel cell to the reformer.

6. A method according to claim 5, wherein the heat conveying means comprises a conduit arranged to convey fluid.

7. A method according to claim 1, wherein the reforming reaction is performed in a reformer and methanol is injected into the reformer.

8. A method according to any of the preceding claims, wherein methanol is evaporated prior to undergoing the reforming reaction.

9. A method according to claim 1, wherein the anode of the fuel cell is provided in an anode compartment and the reforming reaction is performed within the anode compartment.

10. A method according to claim 9, wherein methanol is injected into the anode compartment.

11. A method substantially as hereinbefore described with reference to the accompanying drawings.

12. An intermediate-temperature solid oxide fuel cell system comprising:

an intermediate temperature solid oxide fuel cell including an anode and a cathode separated by an electrolyte;

a reformer for reforming methanol to generate hydrogen to be supplied to the anode and

the fuel cell and reformer being arranged such that heat generated by the fuel cell when in use is conveyed to the reformer.

13. A system according to claim 12, wherein the reformer is arranged in thermal contact with the fuel cell.

14. A system according to claim 13, wherein the reformer is provided within a fuel cell stack.

15. A system according to claim 14, wherein a plurality of reformers are provided in a fuel cell stack.

16. A system according to claim 12, wherein means are provided to convey heat generated by the fuel cell to the reformer.

17. A system according to claim 16, wherein the heat conveying means comprises a conduit arranged to convey fluid.

18. A system according to any one of claims 12 to 17, wherein the reformer is provided within an anode compartment of the fuel cell.

19. A system according to any of claims 12 to 18, wherein means is provided for supplying methanol and water or a methanol/water mixture to the reformer at a controllable rate.

20. A system according to claim 19, wherein methanol and water or a methanol/water mixture is injected into the reformer or an evaporator connected to the reformer.

21. A system according to any of claims 12 to 20, including a variable speed air compressor and an air flow measurement device by which means air can be supplied to the system at a variable and controlled rate.

22. A system according to any of claims 12 to 21, including an air heater to heat air prior to it being fed to the stack.

23. A system according to any of claims 12 to 22, including an afterburner to mix and burn any fuel gas not consumed in the fuel cell with air.

24. A system substantially as hereinbefore described with reference to the accompanying drawings.

The Patent Office

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Application No: GB 0319137.6
Claims searched: 1-24

Examiner: Stig Albjerg Andersen
Date of search: 16 December 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A	-	US 2001/0010873 A1 (THOM), whole document
A	-	US 4454207 A (FRAIOLI ET AL.), whole document
A	-	US 4374184 A (SOMERS ET AL.), whole document

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{V}:

Worldwide search of patent documents classified in the following areas of the IPC^{7}:

H01M

The following online and other databases have been used in the preparation of this search report:

WPI, EPODOC, JAPIO, TXTUS0, TXTUS1, TXTUS2, TXTUS3, TXTEP1, TXTGB1, TXTWO1